



THE UNIVERSITY *of* EDINBURGH

## Edinburgh Research Explorer

### Constant-volume heat capacity in a near-critical fluid from Monte Carlo simulations

**Citation for published version:**

Daub, CD, Camp, PJ & Patey, GN 2004, 'Constant-volume heat capacity in a near-critical fluid from Monte Carlo simulations', *The Journal of Chemical Physics*, vol. 121, no. 18, pp. 8956-8959.  
<https://doi.org/10.1063/1.1795713>

**Digital Object Identifier (DOI):**

[10.1063/1.1795713](https://doi.org/10.1063/1.1795713)

**Link:**

[Link to publication record in Edinburgh Research Explorer](#)

**Document Version:**

Publisher's PDF, also known as Version of record

**Published In:**

The Journal of Chemical Physics

**Publisher Rights Statement:**

Copyright 2004 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.

**General rights**

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

**Take down policy**

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact [openaccess@ed.ac.uk](mailto:openaccess@ed.ac.uk) providing details, and we will remove access to the work immediately and investigate your claim.



## Constant-volume heat capacity in a near-critical fluid from Monte Carlo simulations

Christopher D. Daub, Philip J. Camp, and G. N. Patey

Citation: *J. Chem. Phys.* **121**, 8956 (2004); doi: 10.1063/1.1795713

View online: <http://dx.doi.org/10.1063/1.1795713>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v121/i18>

Published by the AIP Publishing LLC.

---

### Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: [http://jcp.aip.org/about/about\\_the\\_journal](http://jcp.aip.org/about/about_the_journal)

Top downloads: [http://jcp.aip.org/features/most\\_downloaded](http://jcp.aip.org/features/most_downloaded)

Information for Authors: <http://jcp.aip.org/authors>

## ADVERTISEMENT



Explore the **Most Cited**  
Collection in Applied Physics

AIP  
Publishing

# Constant-volume heat capacity in a near-critical fluid from Monte Carlo simulations

Christopher D. Daub

*Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1*

Philip J. Camp

*School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, United Kingdom*

G. N. Patey

*Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1*

(Received 6 July 2004; accepted 28 July 2004)

We consider a near-critical fluid of hard spheres with short-range interactions ( $\sim r^{-6}$ ) and obtain its constant-volume heat capacity  $C_V$  by means of Monte Carlo calculations in the canonical ensemble. The question addressed is whether or not the heat capacities of the finite-size systems studied in simulations can provide a reliable indication of nonclassical criticality. For the model fluid considered here this is found to be the case. The heat capacity along the critical isochore shows a peak near the critical temperature, with a system size dependence that is consistent with the known Ising universality class of the model. The relevance of our results to recent attempts to determine the universality class of ionic fluids through calculations of  $C_V$  is briefly discussed. © 2004 American Institute of Physics. [DOI: 10.1063/1.1795713]

## I. INTRODUCTION

Computer simulations yield valuable insights on the structure and dynamics of complex condensed-matter systems, yet some fundamental questions remain to be answered before such techniques become universally applicable. The question that concerns us here is, can simulation estimates of the constant-volume heat capacity provide reliable indications of the universality class to which a given system belongs?

The initial motivation for this work stems from Monte Carlo (MC) studies of liquid-vapor criticality in the restricted primitive model (RPM) of ionic fluids carried out by ourselves<sup>1</sup> and others.<sup>2–8</sup> Taken as a whole, this work has resulted in the critical point of the RPM being known with a high degree of accuracy. In addition, a large amount of evidence from finite-size scaling analyses suggests that the universality class of the RPM is that of the three-dimensional Ising model. However, simulation measurements of the constant volume heat capacity  $C_V$  have differed greatly, with some authors reporting a peak in the heat capacity consistent with Ising criticality,<sup>6</sup> while others found no sign of such behavior.<sup>2,3</sup>

In a recent paper dealing with the RPM and other model fluids,<sup>1</sup> we have demonstrated that the choice of statistical mechanical ensemble employed in the simulations can have large effects on the results obtained. Specifically, we found that estimates of  $C_V$  obtained in the grand-canonical ( $\mu$ VT) ensemble can give peaks near the critical point not only for the RPM, but also for systems known to exhibit classical criticality for which no “divergent” peaks are expected.<sup>9–12</sup> We therefore speculated that these peaks are artifacts arising from the influence of finite system size on the relevant

grand-canonical fluctuations of the energy and the particle number. In contrast, estimates of  $C_V$  obtained in canonical (NVT) simulations gave no hint of a peak for the near-critical RPM, probably due to the suppression of density fluctuations and their coupling with energy fluctuations. These observations explained the qualitatively different results reported in the literature.<sup>2,3,6</sup>

In Ref. 1 we also considered a fluid of hard spheres interacting through a short-range attractive potential decaying as  $r^{-6}$ , where  $r$  is the interparticle separation. Renormalization group<sup>11,12</sup> and integral equation<sup>13,14</sup> studies provide strong evidence that such a system belongs to the 3D-Ising universality class,<sup>15</sup> and this is also supported by the mixed-field finite-size scaling (MFFSS) analysis of grand-canonical simulation data.<sup>16</sup> In our earlier NVT simulations employing relatively small systems,  $C_V$  for the short-ranged potential at the relevant critical density did show weak maxima in the vicinity of the critical temperature. However, due to the proximity of the freezing transition, these peaks could not be unambiguously identified with critical “divergences.” In the present paper we revisit this issue, and carry out a systematic investigation employing larger systems. This allows us to conclude that the peaks observed are clearly associated with the expected critical behavior. Hence, simulation measurements of  $C_V$  can be considered as a reliable indicator of the universality class of these systems. We note that a similar systematic study of  $C_V$  has been carried out for one- and two-dimensional continuous-spin Ising models.<sup>17</sup> In addition, Valleau and Torrie have reported  $C_V$  results consistent with Ising-like behavior for a Lennard-Jones fluid.<sup>2</sup>

TABLE I. Summary of the apparent finite-size critical parameters from the present work, and the bulk ( $L=\infty$ ) critical temperature from Ref. 16.

$L/\sigma$	Range of $T^*$ for Padé fits	$T_c^*(L)$	$C_V/Nk_B$
6	0.30–0.60	$0.384 \pm 0.020$	$9.90 \pm 0.23$
10	0.36–0.60	$0.475 \pm 0.010$	$11.66 \pm 0.45$
12	0.42–0.60	$0.501 \pm 0.010$	$12.47 \pm 0.64$
17	0.45–0.60	$0.534 \pm 0.010$	$13.5 \pm 1.3$
22	0.45–0.60	$0.545 \pm 0.010$	$14.2 \pm 1.0$
$\infty$		$0.5972 \pm 0.0001$	

## II. MONTE CARLO COMPUTER SIMULATIONS

The pair potential  $u(r)$  is given by

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon(\sigma/r)^6 & r \geq \sigma, \end{cases} \quad (1)$$

where  $r$  is the pair separation,  $\sigma$  is the hard sphere diameter, and  $\epsilon$  is the well depth. We define a reduced temperature  $T^* = k_B T / \epsilon$  and a reduced density  $\rho^* = N\sigma^3/V$ , where  $N$  is the number of particles and  $V$  is the total volume.

MC simulations in cubic cells of side  $L$  were carried out in the NVT ensemble at densities as close as possible to the critical density [ $\rho_c^* = 0.3757$  (Ref. 16)] and over a temperature range that encompassed the critical temperature [ $T_c^* = 0.5972$  (Ref. 16)]. Periodic boundary conditions were imposed, and the spherical potential was truncated at  $L/2$ . The system sizes considered were  $L/\sigma = 6, 10, 12, 17$ , and  $22$ ; the largest system contained  $N = 4000$  particles in the simulation cell. The systems were well equilibrated at each temperature before statistics were gathered.

For each system size the average configurational energy per particle  $U^{\text{ex}}/N\epsilon$  was obtained as a function of temperature and the results were fitted using a [4,4] Padé approximant,

$$\frac{U^{\text{ex}}}{N\epsilon} = \frac{f_0 + f_1x + f_2x^2 + f_3x^3 + f_4x^4}{1 + g_1x + g_2x^2 + g_3x^3 + g_4x^4}, \quad (2)$$

where  $x = \sqrt{T^*}$ . At low temperatures ( $T^* = 0.3$ – $0.4$ , depending on  $L$ ) there is a “freezing” transition to a solidlike structure which causes a sharp change in the energy; the Padé function cannot accommodate this feature and so we carried out the fitting over restricted temperature ranges as indicated in Table I. The results of the calculations and the fits are shown in Fig. 1. Clearly, the Padé fits provide accurate descriptions of the simulation results.

The canonical heat capacity was calculated in two ways; directly from the fluctuations in energy [ $C_V = (\langle U^2 \rangle - \langle U \rangle^2) / k_B T^2$ ], and through temperature differentiation of the Padé approximant fit to the energy. The results obtained are shown in Fig. 2; the kinetic contribution,  $(3/2)Nk_B$ , has been included. It is apparent that the two methods arrive at similar results, though the fluctuation calculations are subject to larger statistical errors. Also included in Fig. 2 are indications of the apparent finite-size critical temperatures  $T_c^*(L)$  being defined by the positions of the maxima in  $C_V$ ; these values are also given in Table I.

In the thermodynamic limit the heat capacity of an Ising-like system in three dimensions should diverge near  $T_c^*$  with

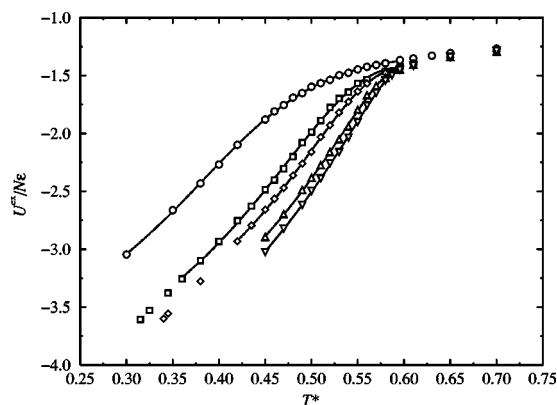


FIG. 1. The average configurational energy per particle,  $U^{\text{ex}}/N\epsilon$ , as a function of  $T^*$  for all system sizes (points), and the respective [4,4] Padé fits (lines):  $L/\sigma = 6$  (circles);  $L/\sigma = 10$  (squares);  $L/\sigma = 12$  (diamonds);  $L/\sigma = 17$  (up triangles);  $L/\sigma = 22$  (down triangles).

an exponent  $\alpha \approx 0.11$  (Ref. 18). According to the finite-size scaling analysis,<sup>19</sup> in a finite system this divergence is replaced with a rounded peak with a maximum at a temperature  $T_c^*(L)$  somewhat removed from the bulk-system critical temperature  $T_c^*(\infty)$  with the peak getting sharper as the system size increases. In the canonical ensemble the position of this peak should scale with system size like,<sup>20</sup>

$$T_c^*(L) = T_c^*(\infty) + a_1 L^{-1/\nu} (1 + a_2 L^{-\theta/\nu} + a_3 L^{-2\beta/\nu}), \quad (3)$$

where  $a_n$  are nonuniversal constants. For an Ising-like critical point,  $\nu \approx 0.630$ ,<sup>18</sup>  $\theta \approx 0.54$ ,<sup>21</sup> and  $\beta \approx 0.326$  (Ref. 18) are the correlation length, Wegner correction-to-scaling,<sup>22</sup> and order-parameter critical exponents, respectively. The last two terms in brackets in Eq. (3) have exponents of similar magnitudes, being  $\theta/\nu \approx 0.86$  and  $2\beta/\nu \approx 1.03$ . The number and range of system sizes considered in this work are not sufficient to fit both of the coefficients  $a_2$  and  $a_3$  reliably, and so we have used an approximate expression for  $T_c^*(L)$  with a single correction-to-scaling term, i.e.,

$$T_c^*(L) = T_c^*(\infty) + a_1 L^{-1/\nu} (1 + a_2 L^{-1}). \quad (4)$$

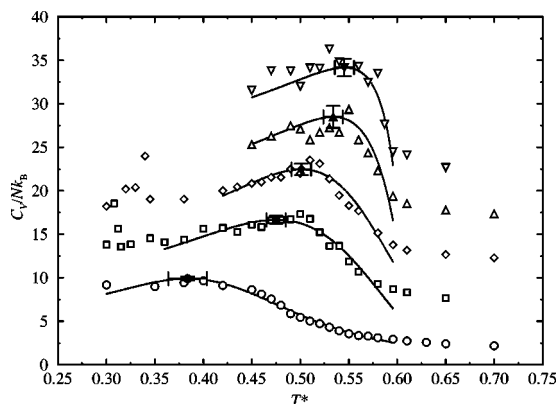


FIG. 2.  $C_V/Nk_B$  as a function of  $T^*$  for all system sizes, calculated directly from the fluctuations in energy (open symbols) and from the derivative of the Padé fits to the average energies (lines):  $L/\sigma = 6$  (circles);  $L/\sigma = 10$  (squares);  $L/\sigma = 12$  (diamonds);  $L/\sigma = 17$  (up triangles);  $L/\sigma = 22$  (down triangles). The solid symbols indicate  $T_c^*(L)$ . The results for each system size are displaced by five units along the ordinate for clarity.



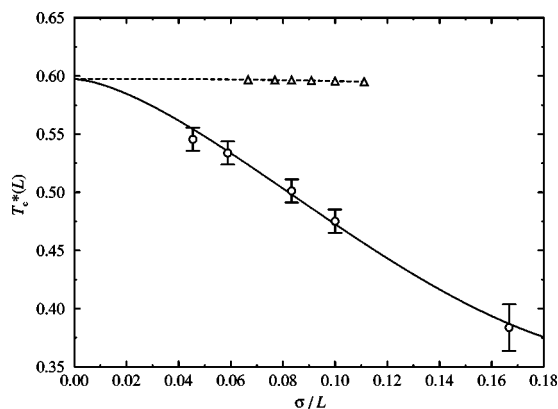


FIG. 3. Apparent finite-size critical temperature,  $T_c^*(L)$ , as a function of  $\sigma/L$ : present simulation results (circles) and fit [Eq. (4)] with  $T_c^*=0.5972$  (Ref. 16); MFFSS results (triangles) and fit [Eq. (5) of Ref. 16] (dashed line).

In Fig. 3 we plot  $T_c^*(L)$ —obtained from the peaks in  $C_V$ —as a function of  $\sigma/L$ . Simulation results obtained from a MFFSS analysis,<sup>16</sup> and the appropriate fit [Eq. (5) in Ref. 16] are included for comparison. The finite-size corrections in the current analysis are clearly much greater than in the MFFSS case. In order to show consistency between our finite-size simulation results and the Ising-like finite-size corrections in Eq. (4), we have performed a fit with the bulk critical temperature being fixed at the value obtained from a MFFSS study,<sup>16</sup>  $T_c^*(\infty)=0.5972$ . The fit parameters are  $a_1 = -6.63(39)$  and  $a_2 = -2.73(32)$ ; the resulting curve is included in Fig. 3. We have also carried out a fit with  $T_c^*(\infty)$  being an additional adjustable parameter, which gives  $T_c^*(\infty)=0.5808(43)$ ,  $a_1 = -4.96(47)$ , and  $a_2 = -1.89(36)$ . This estimate of  $T_c^*(\infty)$  is about 3% lower than that obtained from the MFFSS analysis. Clearly, in the present situation, the  $C_V$  route to the finite-size critical parameters is not reliable for estimating  $T_c^*(\infty)$ , largely because of the pronounced finite-size corrections and the large statistical uncertainties associated with calculating  $C_V$  (either by differentiating  $U$ , or by using the fluctuation formula). Nonetheless, the results show that the finite-size scaling of  $T_c^*(L)$  is at least consistent with Ising-like criticality.

We now turn to a finite-size scaling analysis of the peak height of  $C_V$ . The values of  $C_V$  at  $T=T_c^*(L)$  are reported in Table I, and the reciprocals are plotted in Fig. 4 as a function  $\sigma/L$ . We have fitted curves of the form,

$$\frac{C_V}{Nk_B} = b(L + \delta L)^{a/\nu}, \quad (5)$$

where  $b$  is a nonuniversal constant, and  $\delta L$  is an aid to extrapolation<sup>23</sup> which accounts for corrections to scaling, albeit in an approximate manner. When the exponent ratio  $a/\nu$  is fixed at its Ising value ( $a/\nu \approx 0.175$ ) the fit parameters obtained are  $b=8.506(60)$  and  $\delta L = -3.63(12)$ ; the resulting curve is shown in Fig. 4 and provides a good description of the simulation results. When  $a/\nu$  is treated as an adjustable parameter the results are  $a/\nu=0.189(28)$ ,  $b=8.17(65)$ , and  $\delta L = -3.26(75)$ ; the value of  $a/\nu$  is very close to the Ising value, but this agreement is likely to be

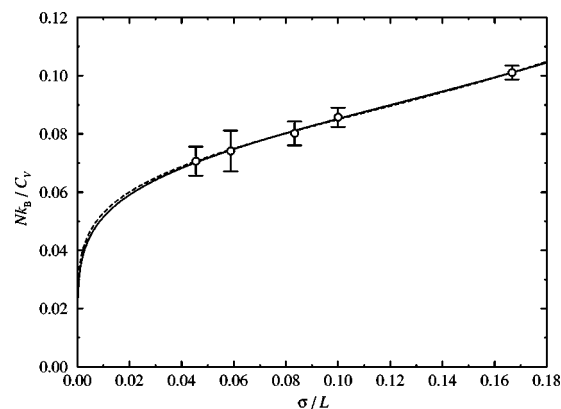


FIG. 4. Reciprocal of the peak height of  $C_V/Nk_B$  at  $T^*=T_c^*(L)$  as a function of  $\sigma/L$ : present simulation results (circles); from Eq. (5) with  $\nu = 0.189(28)$  (solid line); from Eq. (5) with  $\nu=0.175$  (dashed line).

fortuitous. Nonetheless, Fig. 4 shows that the corresponding curve is of comparable quality to that obtained with the Ising value of  $a/\nu$ . These results serve to demonstrate that measurements of thermodynamic properties near the critical point in canonical ensemble simulations can be used to discriminate between classical and nonclassical criticality. Recall that for a classical critical point  $\alpha=0$  and hence the peak-height of  $C_V$  is not expected to increase with increasing system size. Despite the sizable statistical errors in  $C_V$ , Fig. 4 shows that the observed finite-size scaling is at least consistent with Ising-like criticality.

### III. SUMMARY AND CONCLUSIONS

We have investigated the behavior of  $C_V$  in a near-critical fluid of hard spheres with an attractive interaction proportional to  $r^{-6}$ . Our simulations, carried out in the canonical ensemble, show the expected finite-size scaling behavior for a system belonging to the Ising universality class;  $C_V$  clearly has a peak near  $T_c^*(\infty)$  which increases in height and moves closer to  $T_c^*(\infty)$  with increasing system size. The finite-size dependence of the apparent critical temperature is much stronger than that observed in a MFFSS analysis.<sup>16</sup> This is most likely due to the strong suppression of density fluctuations that is inherent to the canonical ensemble. For this reason, the estimate of  $T_c^*(\infty)$  obtained using grand-canonical ensemble simulations and the MFFSS method<sup>16</sup> would appear to be more trustworthy (subject to the effects of pressure mixing being small<sup>24,25</sup>).

We have demonstrated that with sufficient care, direct measurements of  $C_V$  by simulation can indeed be used to rule out classical criticality for a continuous, three dimensional fluid interacting with a short-range potential. The important question remains, however, why similar investigations of model ionic systems show no such peak. The most prosaic explanation is simply that, despite ionic screening, the long-range Coulombic interactions suppress critical energy fluctuations in the “small” systems simulated to date. This explanation is supported by the fact that the MFFSS analyses of the ionic systems show very small finite-size effects and no deviations from Ising-type criticality, just as the MFFSS analysis of the present system shows far smaller

finite-size effects than the analysis of  $C_V$ . The recent study of the RPM by Caillol *et al.*<sup>7</sup> extending up to  $L/\sigma=34$  suggests that the question of the lack of a “diverging”  $C_V$  peak may not be resolved by simulations, at least not without an order of magnitude increase in system size.

## ACKNOWLEDGMENTS

P.J.C. would like to thank Professor M. E. Fisher for a valuable discussion. This research was enabled by the use of WestGrid computing resources, which were funded in part by the Canada Foundation for Innovation, Alberta Innovation and Science, BC Advanced Education, and the participating research institutions. WestGrid equipment was provided by IBM, Hewlett Packard, and SGI. The financial support of the National Science and Engineering Research Council of Canada is gratefully acknowledged.

- <sup>1</sup>C. D. Daub, P. J. Camp, and G. N. Patey, J. Chem. Phys. **118**, 4164 (2003).
- <sup>2</sup>J. Valleau and G. Torrie, J. Chem. Phys. **108**, 5169 (1998).
- <sup>3</sup>J. Valleau and G. Torrie, J. Chem. Phys. **117**, 3305 (2002).
- <sup>4</sup>Q. Yan and J. J. de Pablo, J. Chem. Phys. **111**, 9509 (1999).
- <sup>5</sup>G. Orkoulas and A. Z. Panagiotopoulos, J. Chem. Phys. **110**, 1581 (1999).

- <sup>6</sup>E. Luijten, M. E. Fisher, and A. Z. Panagiotopoulos, J. Chem. Phys. **114**, 5468 (2001).
- <sup>7</sup>J.-M. Caillol, D. Levesque, and J.-J. Weis, J. Chem. Phys. **116**, 10794 (2002).
- <sup>8</sup>E. Luijten, M. E. Fisher, and A. Z. Panagiotopoulos, Phys. Rev. Lett. **88**, 185701 (2002).
- <sup>9</sup>G. Stell, Phys. Rev. B **5**, 981 (1972).
- <sup>10</sup>G. Stell, Phys. Rev. B **8**, 1271 (1973).
- <sup>11</sup>M. E. Fisher, S.-K. Ma, and B. G. Nickel, Phys. Rev. Lett. **29**, 917 (1972).
- <sup>12</sup>J. Sak, Phys. Rev. B **8**, 281 (1973).
- <sup>13</sup>G. Stell, Phys. Rev. Lett. **20**, 533 (1968).
- <sup>14</sup>G. Stell, Phys. Rev. B **1**, 2265 (1970).
- <sup>15</sup>J. Hubbard and P. Schofield, Phys. Lett. **40A**, 245 (1972).
- <sup>16</sup>P. J. Camp and G. N. Patey, J. Chem. Phys. **114**, 399 (2001).
- <sup>17</sup>E. Bayong and H. T. Diep, Phys. Rev. B **59**, 11919 (1999).
- <sup>18</sup>R. Guida and J. Zinn-Justin, J. Phys. A **31**, 8103 (1998).
- <sup>19</sup>M. N. Barber, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1983), Vol. 8, Chap. 2.
- <sup>20</sup>Y. C. Kim and M. E. Fisher, Phys. Rev. E **68**, 041506 (2003).
- <sup>21</sup>J. H. Chen, M. E. Fisher, and B. G. Nickel, Phys. Rev. Lett. **48**, 630 (1982).
- <sup>22</sup>F. J. Wegner, Phys. Rev. B **5**, 4529 (1972).
- <sup>23</sup>G. Orkoulas, A. Z. Panagiotopoulos, and M. E. Fisher, Phys. Rev. E **61**, 5930 (2000).
- <sup>24</sup>Y. C. Kim, M. E. Fisher, and G. Orkoulas, Phys. Rev. E **67**, 061506 (2003).
- <sup>25</sup>Y. C. Kim and M. E. Fisher, J. Phys. Chem. B **108**, 6750 (2004).